

# ON AN INTERPRETATION OF THE LIMITS OF PRE-DISSOCIATION IN THE SPECTRUM OF CARBON MONOXIDE AND THE LATENT HEAT OF SUBLIMATION OF GRAPHITE \*

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(Received for publication, April 12, 1951)

**ABSTRACT.** From a survey of the available data on predissociation phenomena in carbon monoxide, the energy of dissociation into C ( $^3P$ ) and O ( $^3P$ ) atoms has been found to be 8.87 volts. This assignment gives the latent heat of sublimation of graphite into C ( $^3P$ ) atoms as 118.74 kcal. These figures give a satisfactory account of the known experimental results. It has also been shown that the average energy of the C-H bond in methane, calculated with the results for graphite, is of the right order.

## I

The spectrum of the carbon monoxide molecule is well known but the convergence limit of the ground state  $X\ ^1\Sigma^+$  (figure 1), which specifies the energy of dissociation of the molecule into C ( $^3P$ ) and O ( $^3P$ ) atoms has not been located yet with certainty. Data for the vibrational levels of the  $X\ ^1\Sigma^+$  state are available only up to  $v=25$  corresponding to an energy level of 5.6 volts, which is nowhere near the dissociation continuum. The Birge-Sponer extrapolation method leads usually to an upper limit, and therefore the value 11.34 volts obtained for this state by extrapolation over a long range with the few known vibrational levels has been discarded by other workers as being 20 to 40 % high. (Herzberg, 1944).

In the spectrum of a molecule, the predissociation and dissociation limits are known to give an idea of the products of dissociation of the states involved, and the different combinations of the atomic states in which they occur. Consequently, a scrutiny of the energy differences of the various limits enables us to identify the one which represents the energy of dissociation of the ground state. An estimate made with reference to a predissociation limit is considered fairly accurate, provided predissociation is established without any ambiguity. A mere weakening of the intensity of a few bands unless backed by other evidence may be misleading.

## II

### *Available data on Predissociation.*

From a study of the predissociation phenomena in the spectrum of CO, many workers in the field (Schmid and Gerö, 1937, 1938; Herzberg 1937; Gaydon and Penney, 1944; Hagstrum, 1947; Valatin, 1948; Springall,

\* Communicated by Prof. M N, Saha.

1950) have assigned different values to  $D(\text{CO})$ , with the support of evidence available from electron impact experiments, photo-dissociation of CO, thermochemical data and direct experimental measurements on the sublimation of graphite. The various limits of predissociation established by different investigators are reproduced in Table I.

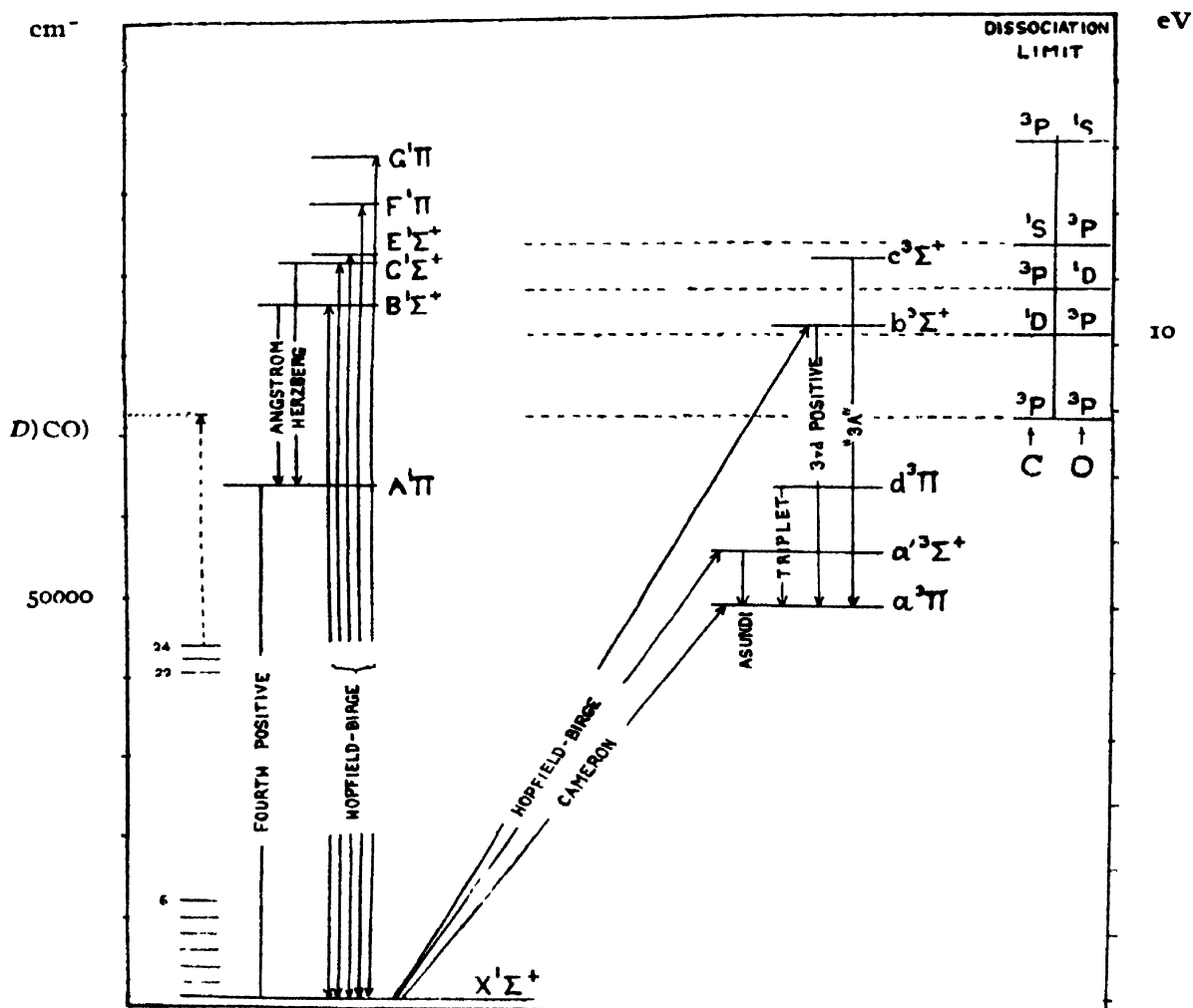


FIG. 1  
Energy levels of CO

There is good deal of controversy as regards the interpretation and assignment of the levels of the various predissociation effects; in fact, some of these are not considered true predissociations at all (Hagstrum, 1947; Herzberg, 1937; Gaydon and Penney, 1944). For instance, Gaydon and Penney (1944) have observed that as the " $3A$ " bands are superposed on the fourth positive system, anomalous intensities in the lines of the latter are not unlikely, and may have the appearance of predissociation. According to Hagstrum (1947), the predissociation in  $B^1\Sigma^+$  and  $b^3\Sigma^+$ , observed at 11.11 volts, is maximum for the potential curve of the  $a^3\Sigma^+$  state (which predissociates the former two), the true dissociation limit being estimated

TABLE I

Predissociation limits in CO spectrum

Limits in volts above $X^1\Sigma^+$	Band System	Nature of Effect
6.89 (Schmid & Gerö)	Cameron [ $a^3\Pi \rightarrow X^1\Sigma^+$ ]	Intensity break off in vibrational structure of $a^3\Pi$ state.
8.19 (Schmid & Gerö)	Asundi [ $a'^3\Sigma^+ \rightarrow a^3\Pi$ ]	Intensity break off in vibrational structure of $a'^3\Sigma^+$ state.
8.87 (Schmid & Gerö)	Triplet [ $d^3\Pi \rightarrow a^3\Pi$ ]	Intensity break off in vibrational structure of $d^3\Pi$ state
8.87 (Schmid & Gerö)	Angstrom [ $B^1\Sigma^+ \rightarrow A^1\Pi$ ]	Predissociation in $A^1\Pi$ state
9.6 (Schmid & Gerö)	Fourth Positive [ $A^1\Pi \rightarrow X^1\Sigma^+$ ]	Predissociation in $A^1\Pi$ state, probably accidental predissociation or only perturbation.
9.14 (Herzberg)		
10.13 (Schmid & Gerö)	Fourth Positive.	Predissociation in $A^1\Pi$ state.
10.87 (Hagstrum)	Angstrom [ $B^1\Sigma^+ \rightarrow A^1\Pi$ ] Third Positive, [ $b'^3\Sigma^+ \rightarrow a^3\Pi$ ]	Predissociation in $B^1\Sigma^+$ and $b'^3\Sigma^+$ states, by $a'^3\Sigma^+$ state. The potential maximum of $a'^3\Sigma^+$ state lies at 11.11 volts, the true limit being situated at 10.87 volts (Hagstrum, 1947).
11.55 (Schmid & Gerö)	Herzberg [ $C^1\Sigma^+ \rightarrow A^1\Pi$ ] "3A" [ $c^3\Sigma^+ \rightarrow a^3\Pi$ ] Hopfield-Birge [ $E^1\Sigma^+ \rightarrow X^1\Sigma^+$ ]	Predissociation in $C^1\Sigma^+$ , $c^3\Sigma^+$ , $E^1\Sigma^+$ states respectively.
12.9 $\pm$ 0.3 (Howell)	Hopfield-Birge [ $F^1\Pi \rightarrow X^1\Sigma^+$ ]	Extrapolated term convergence in $F^1\Pi$ state, with a possible error of 0.3 volt (Howell, 1949)

to be 10.87 volts. The effect at 9.6 volts is probably doubtful, as Herzberg (1937) has observed that the nature of weakening of a few vibrational lines may indicate accidental predissociation or only perturbation instead of real predissociation.

In view of the above, it is proposed to consider the effects at 8.87, 10.13, 10.87, 11.55 and 12.9 volts, as the rest appear to be doubtful.

### III

#### *Value Proposed for D(CO)*

It is known from the experiments of Faltings, Groth and Harteck (1938) that light of  $\lambda$  1470 Å is not able to dissociate CO. This means that the value of  $D(\text{CO})$  is higher than 8.44 volts corresponding to  $\lambda$  1470 Å, and supports the view that the effects listed below 8.44 volts in Table I are not real predissociations. The same absorption experiments also show that light of  $\lambda$  1295 Å (corresponding to 9.57 volts) is able to dissociate CO, thereby providing us with a range 8.44–9.57 within which the value of  $D(\text{CO})$  must lie. As will be seen from Table I that within this range there is only one value, *viz.*, 8.87 volts, which obviously is the figure for  $D(\text{CO})$ .

This deduction apparently does not agree with the results of Kenty, Aicher, Noel, Paritsky and Paolino (1946), who found that metastable xenon atoms with an excitation energy of 9.4 volts failed to dissociate CO. Valatin

(1948), however, feels that this value does not give a lower limit for  $D(\text{CO})$ , as dissociation by collision is a function of transition probability.

With the assignment of  $D(\text{CO}) = 8.87$  volts, the various levels corresponding to dissociation of CO into products with different combinations of atomic states may now be calculated with the known atomic term values of carbon and oxygen (Bacher and Goudsmidt; Shenstone, 1947) given in Table II.

TABLE II

Atomic term differences of carbon and oxygen

Carbon $1s^2 2s^2 2p^2$	Oxygen $1s^2 2s^2 2p^4$
$s^2 p^2 \ ^3P - s^2 p^2 \ ^1D = 1.26$ volts	$s^2 p^4 \ ^3P - s^2 p^4 \ ^1D = 1.96$ volts
$s^2 p^2 \ ^3P - s^2 p^2 \ ^1S = 2.67$ „	$s^2 p^4 \ ^3P - s^2 p^4 \ ^1S = 4.17$ „
$s^2 p^2 \ ^3P - s p^3 \ ^5S = 4.16$ „	

The results have been given in Table III, in the last column of which the observed limits from Table I have been reproduced for comparison.

TABLE III

Calculated limits on the basis  $D(\text{CO}) = 8.87$  volts

Dissociation scheme	Calculated limits above $X \ ^1\Sigma^+$ in volts	Observed limits in volts.
$\text{C}(^3P) + \text{O}(^3P)$	—	8.87
$\text{C}(^1D) + \text{O}(^3P)$	10.13	10.13
$\text{C}(^3P) + \text{O}(^1D)$	10.83	10.87
$\text{C}(^1S) + \text{O}(^3P)$	11.54	11.55
$\text{C}(^3P) + \text{O}(^1S)$	13.04	12.9

It is obvious that the dissociation scheme proposed by the author with  $D(\text{CO}) = 8.87$  volts explains the observed results satisfactorily.

## IV

Value of  $L(\text{C})$

Taking  $D(\text{CO}) = 8.87$  volts the value of  $L(\text{C})$ , latent heat of sublimation of graphite into  $\text{C}(^3P)$  atoms is obtained from the following thermochemical equations.

$$\begin{array}{ll}
 \text{From heat of formation} & \text{CO} + 27.2 \text{ kcal} = [\text{C}] + \frac{1}{2}\text{O}_2 \\
 \text{From heat of dissociation} & \\
 \text{of O}_2 \text{ (Spectroscopic value)} & \frac{1}{2}\text{O}_2 + 58.6 \text{ kcal} = \text{O}({}^3\text{P}) \\
 \text{By definition} & [\text{C}] + L(\text{C}) = \text{C}({}^3\text{P}) \\
 & \text{CO} + D(\text{CO}) = \text{C}({}^3\text{P}) + \text{O}({}^3\text{P}) \\
 \\ 
 \text{Adding} & L(\text{C}) = D(\text{CO}) - 85.80 \text{ kcal.} \\
 & = 204.54 - 85.80 \quad ,, \\
 & = 118.74 \quad ,,
 \end{array}$$

It is worthwhile comparing this result with the figures available from the experiments on the sublimation of graphite. The experimentally determined values of  $L(\text{C})$  cover a wide range, (Springall, 1950). There is a set of low values near 120-125 kcal, and at the highest limit values up to 170-210 kcal (Goldfinger and Jeunehomme, 1936; Marshall and Norton, 1937; Vaughan and Kistiakowsky, 1932) have been claimed. Some of the investigators have supported the higher values at about 170 kcal (Long and Norrish, 1946; Valatin, 1948) on the assumption that graphite requires this amount of energy to vaporize into  $\text{C}(s^2p^3\text{}^5\text{S})$  atoms. The presence of the  ${}^5\text{S}$  state of carbon in equilibrium vapour pressure measurements has, however, been questioned (Shenstone, 1947; Hagstrum, 1947; Springall, 1950) on the ground that this state is not a metastable state. In the opinion of the majority of the investigators  $L(\text{C})$  is less than 140 kcal, but the adoption of a single value for the sublimation of carbon does not fully account for the higher figures obtained by direct measurements.

If it is postulated that the lowest figures ( $\sim 120$  kcal.) available from the experiments on the sublimation of graphite correspond to its vaporization into  $\text{C}({}^3\text{P})$  atoms, the higher figures can be explained by assuming that under different experimental conditions the products of sublimation of graphite are  $\text{C}(s^2p^2\text{}^1\text{D})$  and  $\text{C}(s^2p^2\text{}^1\text{S})$  atoms as given in Table IV.

TABLE IV

Latent heat of sublimation of graphite, taking  $D(\text{CO})=8.87$  volts.

State of C atom	$1s^2\ 2s^2\ 2p^2$			$1s^2\ 2s\ 2p^3$ ${}^5\text{S}$
	${}^3\text{P}$	${}^1\text{D}$	${}^1\text{S}$	
$L \text{ kcal} \rightarrow$	118.74	147.80	180.31	215.14 kcal

For comparison, calculations for the  ${}^5\text{S}$  state of carbon are given the last column, which disagree with the experimental results. It appears that the  ${}^5\text{S}$  state of carbon does not take part in these measurements.

*Average energy of C-H bond in methane.*

In  $\text{CH}_4$  the 4 C-H bonds require different amounts of energy to get ruptured in succession. From direct measurements of the photobromination

of  $\text{CH}_4$  (Anderson, Kistiakowsky and Van Artsdalen, 1942 ; Kistiakowsky, and Van Artsdalen, 1944) and electron impact experiments (Stevenson, 1942), the energy required to rupture the first C-H bond, denoted as  $D(\text{CH}_3\text{-H})$ , has been found to be  $101 \pm 1$  kcal. The energy required to rupture the successive C-H bonds is lower than this figure (Voge, 1936, 1948). For the last C-H bond, we get from predissociation in  $\text{CH}$ ,  $D(\text{C-H})$  equal to 80 kcal, (Shidei, 1936). Thus on the basis of direct measurements only, the average energy of the C-H bond in  $\text{CH}_4$  lies somewhere between the limits 102 and 80 kcal.

Calculation with the aid of thermochemical equations are expected to give only the average value of the energy of C-H bond in  $\text{CH}_4$ . In the thermochemical cycles it is, however, necessary to make a fundamental assumption as to whether in  $\text{CH}_4$ , tetravalent C is in the  $s^2p^2-^3P$ ,  $^1D$ ,  $^1S$  states or  $sp^3-^5S$  state. As an example, the calculations on the basis that C is in the  $s^2p^2-^3P$  state are given below.

Let  $D(\text{CH}_4)$  represent the total energy required to dissociate  $\text{CH}_4$  into  $\text{C}(^3P)$  atom and 4  $\text{H}(^2S)$  atoms.

$$\text{Then } \text{CH}_4 + D(\text{CH}_4) = \text{C}(^3P) + 4\text{H}$$

$$\text{C}(^3P) = [\text{C}] + L(\text{C})$$

$$4\text{H} = 2\text{H}_2 + 210 \text{ kcal. (spectroscopic value)}$$

$$[\text{C}] + 2\text{H}_2 = \text{CH}_4 + 17.87 \text{ ,, (from heat of formation)}$$

$$\text{Adding } D(\text{CH}_4) = L(\text{C}) + 227.87 \text{ kcal.}$$

$$= 118.74 + 227.87 \text{ ,,}$$

$$= 346.61 \text{ ,,}$$

Therefore average energy of

$$\text{C-H bond} = 86.65 \text{ ,,}$$

Other values calculated on the basis of the C atom being in the  $^1D$ ,  $^1S$ ,  $^5S$  states are given in Table V.

TABLE V

State of carbon atom in $\text{CH}_4$	$1s^2 2s^2 2p^2$			$1s^2 2s^2 2p^3$ $^5S$
	$^3P$	$^1D$	$^1S$	
Average energy of C-H bond in kcal.	86.65	93.92	102.04	110.75

As the average value of the energy of C-H bond in methane cannot be higher than 102 kcal., it appears that the assumption made in the last column is not valid. It would be more justified if we assume that in  $\text{CH}_4$  the tetravalent C atom is in the  $^3P$ ,  $^1D$  or  $^1S$  state of the configuration  $1s^2 2s^2 2p^2$ .

Voge's (1936, 1948) calculations for  $\text{CH}_4$  also show that the " $^5\text{S}$  level does not properly measure the energy of the carbon atom in the quadrivalent state"

# ACKNOWLEDGMENTS

The author's thanks are due to the authorities of the Indian Association for the Cultivation of Science, Calcutta, and to Professor D. M. Bose, Director, Bose Research Institute, Calcutta for giving him library facilities for this investigation.

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